REPORT DOCUMENTATION PAGE

AFRL-SR-BL-TR-98-

0393

1. AGENCY USE ONLY (*Leave Blank*)

2. REPORT DATE

April 8, 1998

3. REPORT TYPE AND DATES COVERED

Final Report 11/1/96 - 10/31/97

4. TITLE AND SUBTITLE

"Fundamental Studies of Ions and Ionic Processes"

5. FUNDING NUMBERS

61102F2303B3

2303/FS

61102F

6. AUTHORS

Henry F. Schaefer III

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

Georgia University Research Foundation, Inc.
Boyd Graduate Studies Research Center
Athens, GA 30602

8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)

Dr. Michael R. Berman, Program Manager
AFOSR/NL
110 Duncan Avenue, Suite B115
Bolling Air Force Base, Washington, D.C. 20332-0001

10. SPONSORING / MONITORING AGENCY REPORT NUMBER

F49620-95-1-0059

11. SUPPLEMENTARY NOTES

12a. DISTRIBUTION / AVAILABILITY STATEMENT

APPROVED FOR PUBLIC RELEASE;
DISTRIBUTION UNLIMITED

12b. DISTRIBUTION CODE

13. ABSTRACT (*Maximum 200 words*)

The *object* of this research is to characterize the energetics, spectroscopic properties, and elementary chemical reactions of molecular ions. The approach used will exploit recent developments in *ab initio* molecular quantum mechanics. Some of the systems to be studied include the species CF_n and (n=1-3), SF_n and (n=1-7), $(HNO_3)_n$ $(H_2O)_m$, $(ClNO_3)$, $(H_2SO_4)_m$ $(HNO_3)_n$ $(H_2O)_o$, and + CH_4.

19980430 115

14. SUBJECT TERMS

Ab Initio, computational chemistry, quantum chemistry, theoretical chemistry, molecular ions, ionic processes

15. NUMBER OF PAGES

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT

18. SECURITY CLASSIFICATION OF THIS PAGE

19. SECURITY CLASSIFICATION OF ABSTRACT

20. LIMITATION OF ABSTRACT

Final Technical Report

Air Force Office of Scientific Research

Grant AFOSR-95-1-0059

"Fundamental Studies of Ions and Ionic Processes"

Principal Investigator: Henry F. Schaefer III

Center for Computational Quantum Chemistry

University of Georgia

I. Summary

The primary thrust of this research during the past three years has been toward the reliable prediction of the electron affinities of molecular species of atmospheric interest. The research has produced many important practical results, for example the electron affinities of all the simple fluorocarbons, chlorine fluorides, and bromine fluorides. Moreover, we have developed theoretical methods that can reliably predict the electron affinities of much larger molecules. Indeed, our computational proof that density functional theory is applicable to negative ions is one of the most surprising results to emerge from electronic structure theory in recent years.

II. Publications Supported by the Grant

(November 1, 1994 - October 31, 1997).

1. Y. Xie and H. F. Schaefer, "The Electron Affinity of CF", *J. Chem. Phys.* **101**, 10191 (1994).
2. C. M. B. Marsh and H. F. Schaefer, "Trimethylamine Alane and its Dissociation Products" *J. Phys. Chem.* **99**, 195 (1995).
3. T. D. Crawford, K. W. Springer, and H. F. Schaefer, "A Contribution to the Understanding of the Structure of Xenon Hexafluoride", *J. Chem. Phys.* **102**, 3307 (1995).
4. M. L. Leininger, C. D. Sherrill, and H. F. Schaefer, "N_8: A Structure Analogous to Pentalene and Other High Energy Density Minima," *J. Phys. Chem.* **99**, 2324 (1995).
5. B. Ma, C. Meredith, and H. F. Schaefer, "Quest for a Metaphosphate Intermediate - the Mechanisms for Hydrolysis of Pyrophosphates with and without Catalysis", *J. Phys. Chem.* **99**, 3815 (1995).
6. Y. Yamaguchi and H. F. Schaefer, "The $SiOH^+$ - $HSiO^+$ System. A High Level *Ab Initio* Quantum Mechanical Study," *J. Chem. Phys.* **102**, 5327 (1995).
7. B. Ma, Y. Yamaguchi, and H. F. Schaefer, "Spectroscopic Constants and Potential Energy Surfaces for the Possible Interstellar Molecules AlNC and AlCN," *Molecular Physics* **86**, 1331 (1995).
8. P. R. Schreiner, H. F. Schaefer, and P. R. Schleyer "Can AlH_5 Exist?", *J. Chem. Phys.* **103**, 5565 (1995).
9. C. M. B. Marsh and H. F. Schaefer, "Bisammonia Alane Does Not Incorporate Dative Bonds," *J. Phys. Chem.* **99**, 14309 (1995).

10. E. E. Bolton, W. D. Laidig, P. R. Schleyer, and H. F. Schaefer, "Does Singlet 1,1 Dilithioethene Really Prefer a Perpendicular Structure?" *J. Amer. Chem. Soc.* **99**, 17551 (1995).

11. B. Ma, C. L. Collins, and H. F. Schaefer, "Periodic Trends for Transition Metal Dihydrides MH_2, Dihydride Dihydrogen Complexes $MH_2 \bullet H_2$ and Tetrahydrides MH_4 (M = Ti, V, and Cr)", *J. Amer. Chem. Soc.* **118**, 870 (1996).

12. R. A. King, J. M. Galbraith and H. F. Schaefer, "Negative Ion Thermochemistry: The Sulfur Fluorides SF_n/SF_n^- (n=1-7)," *Boys/Shavitt Issue, J. Phys. Chem.* **100**, 6061 (1996).

13. G. S. Tschumper, J. T. Fermann, and H. F. Schaefer, "Structures, Thermochemistry, and Electron Affinities of the PF_n and PF_n^- Series, n = 1 - 6", *J. Chem. Phys.* **104**, 3676 (1996).

14. J. M. Galbraith and H. F. Schaefer, "The Nitrosyl Azide (N_4O) Potential Energy Hypersurface: A High Energy-Density Boom or Bust?" *J. Amer. Chem. Soc.* **118**, 4860 (1996).

15. D. M. Miller, W. D. Allen, and H. F. Schaefer,"The Electron Affinity of CF_3", *Molecular Physics* **88**, 727 (1996).

16. J. M. Galbraith and H. F. Schaefer, "Concerning the Applicability of Density Functional Methods to Atomic and Molecular Negative Ions", *J. Chem. Phys.* **105**, 862 (1996).

17. T. J. Van Huis, J. M. Galbraith, and H. F. Schaefer, "The Monochlorine Fluorides (ClF_n) and their Anions (ClF_n^-), n = 1 - 7: Structures and Energetics", *Molecular Physics* **89**, 607 (1996).

18. R. A. King, V. S. Mastryukov, and H. F. Schaefer, "The Electron Affinities of the Silicon Fluorides SiF_n (n = 1-5)," *J. Chem. Phys.* **105**, 6880 (1996).

19. J. C. Stephens, E. E. Bolton, and H. F. Schaefer, "Quantum Mechanical Vibrational Frequencies and Matrix Isolation Assignments for Al_2H_2", *J. Chem. Phys.*, **107**, 119 (1997).

20. R. A. Morris, W. B. Knighton, A. A. Viggiano, B. C. Hoffman, and H. F. Schaefer, "The Gas Phase Acidity of H_3PO_4", *J. Chem. Phys.* **106**, 3545 (1997).

21. T. J. Van Huis and H. F. Schaefer, "The ClO_4 Radical: Experiment vs. Theory", *J. Chem. Phys.*, **106**, 4028 (1997).

22. J. C. Rienstra and H. F. Schaefer, "Revision of the Experimental Electron Affinity of BO", *J. Chem. Phys.*, **106**, 8278 (1997).

23. A. Tian, F. Ding, L. Zhang, Y. Xie, and H. F. Schaefer, "New Isomers of N_8 without Double Bonds", *J. Phys. Chem. A* **101**, 1946 (1997).

24. M. L. Leininger, T. J. Van Huis, and H. F. Schaefer, "Protonated High Energy Density Materials: The N_4 Tetrahedron and N_8 Octahedron", *J. Phys. Chem.* **101**, 4460 (1997).

25. G. S. Tschumper and H. F. Schaefer, "Predicting Electron Affinities from Density Functional Theory: Some Positive Results for Negative Ions", *J. Chem. Phys.* **107**, 2529 (1997).

26. R. A. King, N. D. Pettigrew, and H. F. Schaefer, "The Electron Affinities of the Perfluorocarbons C_2F_n, n = 1 - 6", *J. Chem. Phys.* **107**, 8536 (1997).

27. J. Gu, K. Chen, Y. Xie, H. F. Schaefer, R. A. Morris, and A. A. Viggiano, "The Electron Affinities of PF and PF_2," *J. Chem. Phys.* **108**, 1050 (1998).

III. List of Participating Professionals

A. Senior Research Personnel:

Professor Henry F. Schaefer III

B. Junior Research Personnel:

Mr. Evan E. Bolton

Mr. Rollin A. King

Mr. Matthew L. Leininger

Ms. Deanna M. Miller

Mr. John M. Galbraith

Mr. Jonathan C. Rienstra

Mr. C. David Sherrill

Mr. Jeffrey C. Stephens

Mr. Gregory S. Tschumper

Mr. Timothy J. Van Huis